

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08F 212/04, 4/64		A1	(11) International Publication Number: WO 97/42241 (43) International Publication Date: 13 November 1997 (13.11.97)
(21) International Application Number: PCT/NL97/00243			(81) Designated States: AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GE, HU, IL, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, TR, TT, UA, US, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).
(22) International Filing Date: 1 May 1997 (01.05.97)			
(30) Priority Data: 96201114.4 3 May 1996 (03.05.96) EP (34) Countries for which the regional or international application was filed: NL et al.			
(71) Applicant (for all designated States except US): DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL).			Published <i>With international search report.</i>
(72) Inventors; and			
(75) Inventors/Applicants (for US only): RENKEMA, Jacob [NL/NL]; Heer Ottostraat 25, NL-6121 NB Bomm (NL). MUSKENS, Bernardus, Johanna [NL/NL]; Gansbeek 64, NL-6166 JB Geleen (NL). VAN BEEK, Johannes, Antonius, Maria [NL/NL]; 75 Tyrella Court, Mountain View, CA 94043 (NL). VAN DOREMEALE, Gerardus, Henricus, Josephus [NL/NL]; Op de Hoef 6, NL-6132 HN Sittard (NL).			
(74) Agent: SCHELTUS, Irma; Octrooibureau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).			

(54) Title: PROCESS FOR THE PREPARATION OF AN ETHYLENE AND α -OLEFIN COPOLYMER

(57) Abstract

The present process preparing an ethylene/ α -olefin copolymer is conducted in the presence of a novel transition metal complex and co-catalyst. The process is further characterizable in that the transition metal complex is a reduced transition metal complex, selectable from groups 4-6 of the Periodic System of the Elements, with a multidentate monoanionic ligand and with two monoanionic ligands, at a temperature of between 100 and 220 °C. In particular the reduced transition metal in the complex is titanium (Ti (III)).

Best Available Copy

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

- 1 -

5 PROCESS FOR THE PREPARATION OF AN
ETHYLENE AND α -OLEFIN COPOLYMER

BACKGROUND OF THE INVENTION

1. FIELD OF THE INVENTION

10 The invention relates to a process for the preparation of an ethylene and α -olefin copolymer with an ethylene content of between about 20 and 90 weight % at a temperature range of 100-220°C, with a catalyst composition comprising a transition metal complex and a 15 co-catalyst.

2. DESCRIPTION OF THE RELATED ART

20 A process for the preparation of an ethylene/ α -olefin copolymer is known from U.S. Patent No. 5,491,207, in which a cyclopentadiene based transition metal complex (in combination with a co-catalyst) is used to prepare ethylene/ α -olefin copolymers having an ethylene content in the range of about 20-90 mol%. Here and hereinafter the term 25 "copolymer" means a polymer formed from two types of monomeric constituents: ethylene and one or more α -olefins.

30 A disadvantage of a process according to U.S. Patent No. 5,491,207 is that it is conducted at relatively low temperatures (-10°C to about 100°C), which cause the process to be less attractive from an economical point of view. There is a need for a process to be conducted at higher temperatures. There is also a 35 need for a higher temperature polymerization process which does not require too high a pressure, otherwise the costs for such a high pressure process could undo the advantages of a high temperature process.

SUMMARY OF THE INVENTION

It is therefore, an object of the present invention to solve the aforementioned problems associated with the related art as well as to address the need expressed above. In accordance with the principles of the present invention, this object is obtained by providing a process for the preparation of an ethylene/α-olefin copolymer with an ethylene content of between about 20 and 90 weight %, at higher temperatures that range from 100°C to 220°C, with a catalyst composition comprising a transition metal complex and a co-catalyst.

Another object of the present invention is the provision of an ethylene/α-olefin copolymer obtained by the means of a polymerization process with utilization of the catalyst composition according to the invention.

In the present process, the polymerization of ethylene and at least one [additional] α-olefin is conducted under effective copolymerization conditions at a temperature of between 100°C and 220°C, under the influence of the present a catalyst composition.

The catalyst composition includes at least one complex comprising a reduced valency transition metal (M) selected from groups 4-6 of the Periodic Table of Elements, a multidentate monoanionic ligand (X), two monoanionic ligands (L), and, optionally, additional ligands (K). More specifically, the complex of the catalyst composition of the present invention represented by the following formula (I):



wherein the symbols have the following meanings:

M a reduced transition metal selected from group 4, 5 or 6 of the Periodic Table of Elements;

X a multidentate monoanionic ligand represented by 5 the formula: $(Ar-R_t-)_nY(-R_t-DR'_n)_q$;

Y a cyclopentadienyl, amido ($-NR'$), or phosphido group ($-PR'$), which is bonded to the reduced transition metal M;

R at least one member selected from the group 10 consisting of (i) a connecting group between the Y group and the DR'_n group and (ii) a connecting group between the Y group and the Ar group, wherein when the ligand X contains more than one R group, the R groups can be identical to or 15 different from each other;

D an electron-donating hetero atom selected from group 15 or 16 of the Periodic Table of Elements;

R' a substituent selected from the group consisting 20 of a hydrogen, hydrocarbon radical and hetero atom-containing moiety, except that R' cannot be hydrogen when R' is directly bonded to the electron-donating hetero atom D, wherein when the multidentate monoanionic ligand X contains more than one substituent R', the substituents R' can 25 be identical or different from each other;

Ar an electron-donating aryl group;

L a monoanionic ligand bonded to the reduced 30 transition metal M, wherein the monoanionic ligand L is not a ligand comprising a cyclopentadienyl, amido ($-NR'$), or phosphido ($-PR'$) group, and wherein the monoanionic ligands L can be identical or different from each other;

K a neutral or anionic ligand bonded to the reduced 35 transition metal M, wherein when the transition metal complex contains more than one ligand K, the ligands K can be identical or different from each

other;

m is the number of K ligands, wherein when the K ligand is an anionic ligand m is 0 for M^{3+} , m is 1 for M^{4+} , and m is 2 for M^{5+} , and when K is a neutral ligand m increases by one for each neutral K ligand;

n the number of the R' groups bonded to the electron-donating hetero atom D, wherein when D is selected from group 15 of the Periodic Table of Elements n is 2, and when D is selected from group 16 of the Periodic Table of Elements n is 1;

q,s q and s are the number of $(-R_t-DR'_n)$ groups and $(Ar-R_t-)$ groups bonded to group Y, respectively, wherein q + s is an integer not less than 1; and

15 t the number of R groups connecting each of (i) the Y and Ar groups and (ii) the Y and DR'_n groups, wherein t is selected independently as 0 or 1.

It has surprisingly been found that a transition metal complex of formula (I) makes it possible to prepare ethylene/α-olefin copolymers at temperatures between 100°C and 220°C, whereas other known catalysts for these types of polymerization do not produce copolymers at temperatures above 100°C (they are only active at temperatures well below 100°C; 25 U.S. Patent No. 5,491,207 discloses temperatures between -10°C and 100°C and shows examples with temperatures between 35°C and 50°C).

The process according to the present invention is suitable for the preparation of copolymers 30 having an M_n (the number-average molecular weight (as determined by SEC-DV (Size Exclusion Chromatography/Differential Viscometry combination)), of as low as about 100. The temperature at which the polymerization is performed is one of the parameters to 35 control the value of M_n . In principle, any ethylene/α-olefin copolymer can be made with an M_n between about

100 and about 500,000.

Copolymers with a molecular weight M_n between about 100 and about 30,000 are preferably prepared in a polymerization process at temperatures between about 135 and about 220°C; copolymers with a molecular weight M_n between about 20,000 and about 100,000 are preferably prepared in a polymerization process at a temperature between about 115 and about 180°C.

The copolymers also have an ethylene content of between about 20 and about 90 weight %. The copolymers can be amorphous, being products with an ethylene content of between about 30 and about 70 weight %, or can be semicrystalline, being products with an ethylene content of between about 70 and about 90 wt %.

The pressure at which the polymerization is conducted is preferably below about 100 MPa. Pressures up to 10 MPa are in several cases sufficient enough for a good catalytic activity. CA-A-2,11,057 discloses a process (in comparative experiment 2) for the preparation of an ethylene/butene low molecular weight copolymer at an extreme high pressure of 1,330 bar to cope with the extreme low catalytic activity at normal pressures.

Other processes known in the art to produce low molecular weight ethylene copolymers either start from high molecular weight products which are broken down in molecular weight (e.g. by shearing) or by using, during the polymerization, an extreme amount of chain regulators (e.g. hydrogen or diethylzinc) for keeping low the molecular weight. In all cases, the temperature at which the copolymers are prepared is as low as -10 - 100°C.

The foregoing and other objects, features, and advantages of the present invention will become

apparent from the following detailed description and claims.

BRIEF DESCRIPTION OF THE DRAWINGS

5 The accompanying drawings illustrate the present invention. In such drawings:

FIG. 1 is a schematic view of a cationic active site of a trivalent catalyst complex in accordance with an embodiment of the present invention;
10 and

FIG. 2 is a schematic view of a neutral active site of a trivalent catalyst complex of a dianionic ligand of a conventional catalyst complex according to WO-A-93/19104.

15

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Various components (groups) of the transition metal complex are discussed below in more detail.

20 (a) The Transition Metal (M)

The transition metal in the complex is selected from groups 4-6 of the Periodic Table of Elements. As referred to herein, all references to the Periodic Table of Elements mean the version set forth 25 in the new IUPAC notation found on the inside of the cover of the Handbook of Chemistry and Physics, 70th edition, 1989/1990, the complete disclosure of which is incorporated herein by reference. More preferably, the transition metal is selected from group 4 of the 30 Periodic Table of Elements, and most preferably is titanium (Ti).

The transition metal is present in reduced form in the complex, which means that the transition metal is in a reduced oxidation state. As referred to 35 herein, "reduced oxidation state" means an oxidation state which is greater than zero but lower than the

highest possible oxidation state of the metal (for example, the reduced oxidation state is at most M^{3+} for a transition metal of group 4, at most M^{4+} for a transition metal of group 5 and at most M^{5+} for a 5 transition metal of group 6).

(b) The X Ligand

The X ligand is a multidentate monoanionic ligand represented by the formula: $(Ar-R_t-)_s Y(-R_t-DR'_n)_q$.
10

As referred to herein, a multidentate monoanionic ligand is bonded with a covalent bond to the reduced transition metal (M) at one site (the anionic site, Y) and is bonded either (i) with a 15 coordinate bond to the transition metal at one other site (bidentate) or (ii) with a plurality of coordinate bonds at several other sites (tridentate, tetradentate, etc.). Such coordinate bonding can take place, for example, via the D heteroatom or Ar group(s). Examples 20 of tridentate monoanionic ligands include, without limitation, $Y-R_t-DR'_{n-1}-R_t-DR'_n$ and $Y(-R-DR'_n)_2$. It is noted, however, that heteroatom(s) or aryl substituent(s) can be present on the Y group without coordinately bonding to the reduced transition metal M, 25 so long as at least one coordinate bond is formed between an electron-donating group D or an electron donating Ar group and the reduced transition metal M.

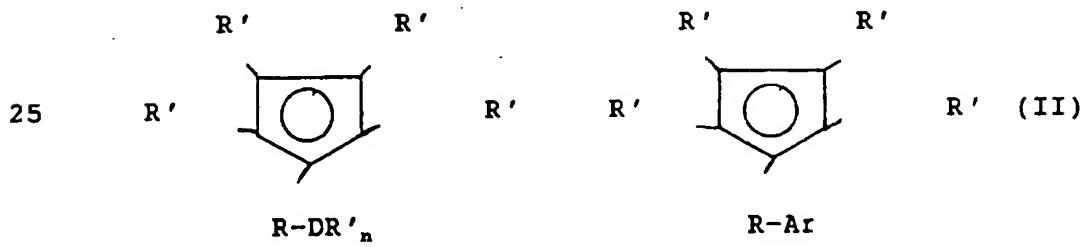
R represents a connecting or bridging group between the DR'_n and Y, and/or between the electron-30 donating aryl (Ar) group and Y. Since R is optional, "t" can be zero. The R group is discussed below in paragraph (d) in more detail.

(c) The Y Group

The Y group of the multidentate monoanionic ligand (X) is preferably a cyclopentadienyl, amido ($-\text{NR}'-$), or phosphido ($-\text{PR}'-$) group.

Examples of a multidentate monoanionic ligand with a Cp group as the Y group (or ligand) include the following (with the $(-R_t-DR'_n)$ or $(Ar-R_t-)$ substituent on the ring):

20

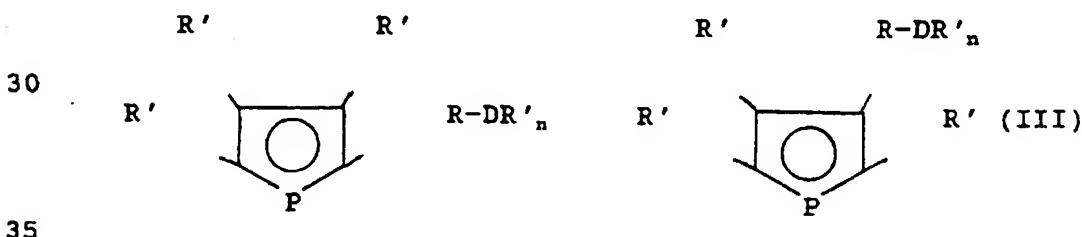


The Y group can also be a hetero cyclopentadienyl group. As referred to herein, a hetero cyclopentadienyl group means a hetero ligand derived from a cyclopentadienyl group, but in which at least one of the atoms defining the five-member ring structure of the cyclopentadienyl is replaced with a hetero atom via an endocyclic substitution. The hetero Cp group also includes at least one $R_t-DR'_n$ group or

R_t-Ar group that replaces one of the hydrogens bonded to the five-member ring of the Cp group via an exocyclic substitution. As with the Cp group, as referred to herein the hetero Cp group encompasses 5 indenyl, fluorenyl, and benzoindenyl groups, and other polycyclic aromatics containing at least one 5-member dienyl ring, so long as at least one of the substituents of the hetero Cp group is an R_t-DR'_n group or R_t-Ar group that replaces one of the hydrogens 10 bonded to the five-member ring of the hetero Cp group via an exocyclic substitution.

The hetero atom can be selected from group 14, 15 or 16 of the Periodic Table of Elements. If 15 there is more than one hetero atom present in the five-member ring, these hetero atoms can be either the same or different from each other. More preferably, the hetero atom(s) is/are selected from group 15, and still more preferably the hetero atom(s) selected is/are phosphorus.

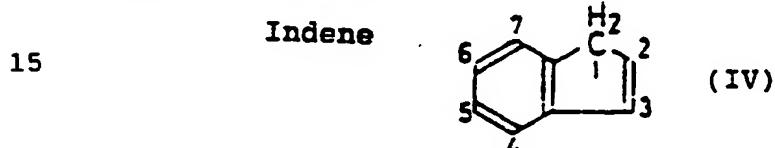
20 By way of illustration and without limitation, representative hetero ligands of the X group that can be practiced in accordance with the present invention are hetero cyclopentadienyl groups having the following structures, in which the hetero 25 cyclopentadienyl contains one phosphorus atom (i.e., the hetero atom) substituted in the five-member ring:



It is noted that, generally, the transition metal group M is bonded to the Cp group via an η^5 bond.

The other R' exocyclic substituents (shown in formula (III)) on the ring of the hetero Cp group can be of the same type as those present on the Cp group, as represented in formula (II). As in formula (II), at 5 least one of the exocyclic substituents on the five-member ring of the hetero cyclopentadienyl group of formula (III) is the R_t-DR'_n group or the R_t-Ar group.

The numeration of the substitution sites of the indenyl group is in general and in the present 10 description based on the IUPAC Nomenclature of Organic Chemistry 1979, rule A 21.1. The numeration of the substituent sites for indene is shown below. This numeration is analogous for an indenyl group:



The Y group can also be an amido (-NR'-) 20 group or a phosphido (-PR'-) group. In these alternative embodiments, the Y group contains nitrogen (N) or phosphorus (P) and is bonded covalently to the transition metal M as well as to the (optional) R group of the (-R_t-DR'_n) or (Ar-R_t-) substituent.

25

(d) The R Group

The R group is optional, such that it can be absent from the X group. Where the R group is absent, the DR'_n or Ar group is bonded directly to the Y group 30 (that is, the DR'_n or Ar group is bonded directly to the Cp, amido, or phosphido group). The presence or absence of an R group between each of the DR'_n groups and/or Ar groups is independent.

Where at least one of the R groups is 35 present, each of the R group constitutes the connecting bond between, on the one hand the Y group, and on the other hand the DR'_n group or the Ar group. The presence and size of the R group determines the accessibility of

the transition metal M relative to the DR'_n or Ar group, which gives the desired intramolecular coordination. If the R group (or bridge) is too short or absent, the donor may not coordinate well due to 5 ring tension. The R groups are each selected independently, and can generally be, for example, a hydrocarbon group with 1-20 carbon atoms (e.g., alkylidene, arylidene, aryl alkylidene, etc.). Specific examples of such R groups include, without limitation, 10 methylene, ethylene, propylene, butylene, phenylene, whether or not with a substituted side chain. Preferably, the R group has the following structure:



15

where p = 1-4. The R' groups of formula (IV) can each be selected independently, and can be the same as the R' groups defined below in paragraph (g).

In addition to carbon, the main chain of the 20 R group can also contain silicon or germanium. Examples of such R groups are: dialkyl silylene (-SiR'₂-), dialkyl germylene (-GeR'₂-), tetra-alkyl silylene (-SiR'₂-SiR'₂-), or tetraalkyl silaethylene (-SiR'₂CR'₂-). The alkyl groups in such a group preferably have 1-4 25 carbon atoms and more preferably are a methyl or ethyl group.

(e) The DR'_n Group

This donor group consists of an electron-donating hetero atom D, selected from group 15 or 16 of the Periodic Table of Elements, and one or more substituents R' bonded to D. The number (n) of R' groups is determined by the nature of the hetero atom D, insofar as n being 2 if D is selected from group 15 30 and n being 1 if D is selected from group 16. The R' substituents bonded to D can each be selected 35

independently, and can be the same as the R' groups defined below in paragraph (g), with the exception that the R' substituent bonded to D cannot be hydrogen.

The hetero atom D is preferably selected from 5 the group consisting of nitrogen (N), oxygen (O), phosphorus (P) and sulphur (S); more preferably, the hetero atom is nitrogen (N). Preferably, the R' group is an alkyl, more preferably an n-alkyl group having 1-20 carbon atoms, and most preferably an n-alkyl having 10 1-8 carbon atoms. It is further possible for two R' groups in the DR'_n group to be connected with each other to form a ring-shaped structure (so that the DR'_n group can be, for example, a pyrrolidinyl group). The DR'_n group can form coordinate bonds with the 15 transition metal M.

(f) The Ar Group

The electron-donating group (or donor) selected can also be an aryl group (C₆R'₅), such as 20 phenyl, toyl, xylyl, mesityl, cumenyl, tetramethyl phenyl, pentamethyl phenyl, a polycyclic group such as triphenylmethane, etc. The electron-donating group D of formula (I) cannot, however, be a substituted Cp group, such as an indenyl, benzoindenyl, or fluorenyl group.

25 The coordination of this Ar group in relation to the transition metal M can vary from η^1 to η^6 .

(g) The R' Group

The R' groups may each separately be hydrogen 30 or a hydrocarbon radical with 1-20 carbon atoms (e.g. alkyl, aryl, aryl alkyl and the like as shown in Table 1).

Examples of alkyl groups are methyl, ethyl, propyl, butyl, hexyl and decyl. Examples of aryl groups are 35 phenyl, mesityl, toyl and cumenyl. Examples of aryl alkyl groups are benzyl, pentamethylbenzyl, xylyl,

styryl and trityl. Examples of other R' groups are halides, such as chloride, bromide, fluoride and iodide, methoxy, ethoxy and phenoxy.

Also, two adjacent hydrocarbon radicals of the Y group

5 can be connected with each other to define a ring system; therefore the Y group can be an indenyl, a fluorenyl or a benzoindenyl group. The indenyl, fluorenyl, and/or benzoindenyl can contain one or more R' groups as substituents. R' can also be a substituent
10 which instead of or in addition to carbon and/or hydrogen can comprise one or more hetero atoms of groups 14-16 of the Periodic Table of Elements. Thus, a substituent can be, for example, a Si-containing group, such as Si(CH₃)₃.

15

(h) The L Group

The transition metal complex contains two monoanionic ligands L bonded to the transition metal M. Examples of the L group ligands, which can be identical 20 or different, include, without limitation, the following: a hydrogen atom; a halogen atom; an alkyl, aryl or aryl alkyl group; an alkoxy or aryloxy group; a group comprising a hetero atom selected from group 15 or 16 of the Periodic Table of Elements, including, by 25 way of example, (i) a sulphur compound, such as sulphite, sulphate, thiol, sulphonate, and thioalkyl, and (ii) a phosphorus compound, such as phosphite, and phosphate. The two L groups can also be connected with each other to form a dianionic bidentate ring system.

30 These and other ligands can be tested for their suitability by means of simple experiments by one skilled in the art.

Preferably, L is a halide and/or an alkyl or aryl group; more preferably, L is a Cl group and/or a 35 C₁-C₄ alkyl or a benzyl group. The L group, however, cannot be a Cp, amido, or phosphido group. In other

words, L cannot be one of the Y groups.

(i) The K Ligand

The K ligand is a neutral or anionic group
5 bonded to the transition metal M. The K group is a
neutral or anionic ligand bonded to M. When K is a
neutral ligand K may be absent, but when K is
monoanionic, the following holds for K_m :

m = 0 for M^{3+}
10 m = 1 for M^{4+}
m = 2 for M^{5+}

On the other hand, neutral K ligands, which
by definition are not anionic, are not subject to the
same rule. Therefore, for each neutral K ligand, the
15 value of m (i.e., the number of total K ligands) is one
higher than the value stated above for a complex having
all monoanionic K ligands.

The K ligand can be a ligand as described
above for the L group or a Cp group ($-C_5R'_5$), an amido
20 group ($-NR'_2$) or a phosphido group ($-PR'_2$). The K group
can also be a neutral ligand such as an ether, an
amine, a phosphine, a thioether, among others.

If two K groups are present, the two K groups
can be connected with each other via an R group to form
25 a bidentate ring system.

As can also be seen from formula (I), the X
group of the complex contains a Y group to which are
linked one or more donor groups (the Ar group(s) and/or
30 DR'_n group(s)) via, optionally, an R group. The number
of donor groups linked to the Y group is at least one
and at most the number of substitution sites present on
a Y group.

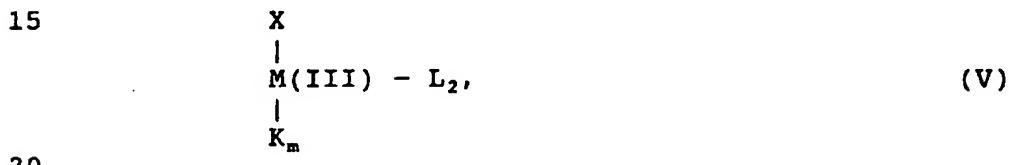
With reference, by way of example, to the
structure according to formula (II), at least one
35 substitution site on a Cp group is made by an R_t -Ar
group or by an R_t -DR'_n group (in which case $q + s = 1$).

If all the R' groups in formula (II) were R_t -Ar groups, R_t -DR'_n groups, or any combination thereof, the value of (q + s) would be 5.

One preferred embodiment of the catalyst

5 composition according to the present invention
comprises a transition metal complex in which a
bidentate/monoanionic ligand is present and in which
the reduced transition metal has been selected from
group 4 of the Periodic Table of Elements and has an
10 oxidation state of +3.

In this case, the catalyst composition according to the invention comprises a transition metal complex represented by formula (V):



where the symbols have the same meaning as described above for formula (I) and where M(III) is a transition metal selected from group 4 of the Periodic Table of Elements and is in oxidation state 3+.

25 Such a transition metal complex has no anionic K ligands (for an anionic K, $m = 0$ in case of M^{3+}).

It should be pointed out that in WO-A-93/19104, transition metal complexes are described in which a group 4 transition metal in a reduced oxidation state (3+) is present. The complexes described in WO-A-93/19104 have the general formula:



35

The Y group in this formula (VI) is a hetero atom, such as phosphorus, oxygen, sulfur, or nitrogen bonded covalently to the transition metal M (see p. 2 of WO-A-

93/19104). This means that the $Cp_a(ZY)_b$ group is of a dianionic nature, and has the anionic charges residing formerly on the Cp and Y groups. Accordingly, the $Cp_a(ZY)_b$ group of formula (VI) contains two covalent bonds: the first being between the 5-member ring of the Cp group and the transition metal M, and the second being between the Y group and the transition metal. By contrast, the X group in the complex according to the present invention is of a monoanionic nature, such that a covalent bond is present between the Y group (e.g., the Cp group) and transition metal, and a coordinate bond can be present between the transition metal M and one or more of the $(Ar-R_t^-)$ and $(-R_t-DR'_n)$ groups. This changes the nature of the transition metal complex and consequently the nature of the catalyst that is active in the polymerization. As referred to herein, a coordinate bond is a bond (e.g., H_3N-BH_3) which when broken, yields either (i) two species without net charge and without unpaired electrons (e.g., $H_3N:$ and BH_3) or (ii) two species with net charge and with unpaired electrons (e.g., H_3N^+ and BH_3^-). On the other hand, as referred to herein, a covalent bond is a bond (e.g., CH_3-CH_3) which when broken yields either (i) two species without net charge and with unpaired electrons (e.g., CH_3^+ and CH_3^-) or (ii) two species with net charges and without unpaired electrons (e.g., CH_3^+ and CH_3^-). A discussion of coordinate and covalent bonding is set forth in Haaland et al. (Angew. Chem Int. Ed. Eng. Vol. 28, 1989, p. 992), the complete disclosure of which is incorporated herein by reference.

The following explanation is proposed, although it is noted that the present invention is in no way limited to this theory.

Referring now more particularly to FIG. 2, the transition metal complexes described in WO-A-93/19104 are ionic after interaction with the co-

catalyst. However, the transition metal complex according to WO-A-93/19104 that is active in the polymerization contains an overall neutral charge (on the basis of the assumption that the polymerizing 5 transition metal complex comprises, a M(III) transition metal, one dianionic ligand and one growing monoanionic polymer chain (POL)). By contrast, as shown in FIG. 1, the polymerization active transition metal complex of the catalyst composition according to the present 10 invention is of a cationic nature (on the basis of the assumption that the polymerizing transition metal complex - based on the formula (V) structure - comprises, a M(III) transition metal, one monoanionic bidentate ligand and one growing monoanionic polymer 15 chain (POL)).

Transition metal complexes in which the transition metal is in a reduced oxidation state, but have the following structure:

20

 $Cp - M(III) - L_2$

(VII)

are generally not active in co-polymerization reactions. It is precisely the presence, in the transition metal complex of the present invention, of 25 the DR'_n or Ar group (the donor), optionally bonded to the Y group by means of the R group, that gives a stable transition metal complex suitable for polymerization.

Such an intramolecular donor is to be 30 preferred over an external (intermolecular) donor on account of the fact that the former shows a stronger and more stable coordination with the transition metal complex.

It will be appreciated that the catalyst 35 system may also be formed in situ if the components thereof are added directly to the polymerization

reactor system and a solvent or diluent, including liquid monomer, is used in said polymerization reactor.

The catalyst composition of the present invention also contains a co-catalyst. For example, the 5 co-catalyst can be an organometallic compound. The metal of the organometallic compound can be selected from group 1, 2, 12 or 13 of the Periodic Table of Elements. Suitable metals include, for example and without limitation, sodium, lithium, zinc, magnesium, 10 and aluminum, with aluminum being preferred. At least one hydrocarbon radical is bonded directly to the metal to provide a carbon-metal bond. The hydrocarbon group used in such compounds preferably contains 1-30, more preferably 1-10 carbon atoms. Examples of suitable 15 compounds include, without limitation, amyl sodium, butyl lithium, diethyl zinc, butyl magnesium chloride, and dibutyl magnesium. Preference is given to organoaluminium compounds, including, for example and without limitation, the following: trialkyl aluminum 20 compounds, such as triethyl aluminum and tri-isobutyl aluminum; alkyl aluminum hydrides, such as di-isobutyl aluminum hydride; alkylalkoxy organoaluminium compounds; and halogen-containing organoaluminium compounds, such as diethyl aluminum chloride, 25 diisobutyl aluminum chloride, and ethyl aluminum sesquichloride. Preferably, linear or cyclic aluminoxanes are selected as the organoaluminium compound.

In addition or as an alternative to the 30 organometallic compounds as the co-catalyst, the catalyst composition of the present invention can include a compound which contains or yields in a reaction with the transition metal complex of the present invention a non-coordinating or poorly 35 coordinating anion. Such compounds have been described for instance in EP-A-426,637, the complete disclosure

of which is incorporated herein by reference. Such an anion is bonded sufficiently unstably such that it is replaced by an unsaturated monomer during the co-polymerization. Such compounds are also mentioned in

5 EP-A-277,003 and EP-A-277,004, the complete disclosures of which are incorporated herein by reference. Such a compound preferably contains a triaryl borane or a tetraaryl borate or an aluminum equivalent thereof. Examples of suitable co-catalyst compounds include,

10 without limitation, the following:

- dimethyl anilinium tetrakis (pentafluorophenyl) borate $[C_6H_5N(CH_3)_2H]^+ [B(C_6F_5)_4]^-$;
- dimethyl anilinium bis (7,8-dicarbaundecaborate)-

15 cobaltate (III);

- tri(n-butyl)ammonium tetraphenyl borate;

- triphenylcarbenium tetrakis (pentafluorophenyl) borate;

- dimethylanilinium tetraphenyl borate;

- tris(pentafluorophenyl) borane; and

20 - tetrakis(pentafluorophenyl) borate.

If the above-mentioned non-coordinating or poorly coordinating anion is used, it is preferable for the transition metal complex to be alkylated (that is, the L group is an alkyl group). As described for

25 instance in EP-A-500,944, the complete disclosure of which is incorporated herein by reference, the reaction product of a halogenated transition metal complex and an organometallic compound, such as for instance triethyl aluminum (TEA), can also be used.

30 The molar ratio of the co-catalyst relative to the transition metal complex, in case an organometallic compound is selected as the co-catalyst, usually is in a range of from about 1:1 to about 10,000:1, and preferably is in a range of from about 35 1:1 to about 2,500:1. If a compound containing or yielding a non-coordinating or poorly coordinating

anion is selected as co-catalyst, the molar ratio usually is in a range of from about 1:100 to about 1,000:1, and preferably is in a range of from about 1:2 to about 250:1.

5 As a person skilled in the art would be aware, the transition metal complex as well as the co-catalyst can be present in the catalyst composition as a single component or as a mixture of several components. For instance, a mixture may be desired
10 where there is a need to influence the molecular properties of the polymer, such as molecular weight and in particular molecular weight distribution.

15 The process according to the invention is suitable for the preparation of semi-crystalline or of amorphous copolymers based on ethylene and an α -olefin.

Besides the ethylene, the copolymer according to the invention comprises one or more α -olefins. In general, such an α -olefin contains 3-25 carbon atoms (although higher α -olefins are also allowable); more 20 preferably, the α -olefin contains 3-10 carbon atoms. The α -olefin has preferably been selected from the group consisting of propylene, butene, isobutene, pentene, 4-methyl pentene, hexene, octene and (α -methyl) styrene. More preferably, the α -olefin is 25 propylene, 1-butene, 1-hexene or 1-octene. Most preferred, the α -olefin is propylene.

As indicated before, the process of the present invention enables the preparation of an ethylene/ α -olefin copolymer with a broad range of 30 molecular weights M_n . An alternative for products with a high molecular weight is the characterisation of the copolymer by its Mooney viscosity (ML_{1+4} , 125°C, as per ASTM D1646). The process of the present invention is able to prepare ethylene/ α -olefin copolymers having an 35 ML_{1+4} , 125°C of between 10 and 150.

The catalyst composition in the process

according to the invention can be used supported or non-supported. The transition metal complex or the co-catalyst can be supported on a carrier. It is also possible that both the transition metal complex and the 5 co-catalyst are supported on a carrier. The carrier material for the transition metal complex and for the co-catalyst can be the same material or a different material. It is also possible to support the transition metal complex and the co-catalyst on the 10 same carrier. The supported catalyst systems of the invention can be prepared as separate compounds, which can be used as such in polymerization reactions or the supported catalyst systems can be formed in situ by in situ methods just before a polymerization reaction 15 starts. The supported catalysts are used mainly in gas phase and slurry processes. The carrier used may be any carrier known as carrier material for catalysts, for instance, finely divided solid porous support, including, but not limited to, or $MgCl_2$, Zeolites, 20 mineral clays, inorganic oxides such as talc, silica (SiO_2), alumina (Al_2O_3), silica-alumina, inorganic hydroxides, phosphates, sulphates, and the like, or resinous support materials such as polyolefins, including polystyrene, or mixtures thereof.

25 The carrier may be used as such, or be modified, for example by silanes, aluminium alkyls, aluminoxanes, and others. The catalyst composition may also be prepared by in-situ methods.

30 Polymerization can be effected in a known manner, in the gas phase as well as in a liquid reaction medium. In the latter case, both solution and suspension polymerization are suitable, while the quantity of transition metal to be used generally is such that its concentration in the dispersion agent 35 amounts to 10^{-6} - 10^{-3} mol/l, preferably 10^{-7} - 10^{-4} mol/l.

Any liquid that is inert relative to the catalyst system can be used as a dispersion agent in the polymerization. One or more saturated, straight or branched aliphatic hydrocarbons, such as butanes, 5 pentanes, hexanes, heptanes, pentamethyl heptane or mineral oil fractions such as light or regular petrol, naphtha, kerosine or gas oil are suitable for that purpose. Aromatic hydrocarbons, for instance benzene and toluene, can be used, but because of their cost as 10 well as on account of safety considerations, it will be preferred not to use such solvents for production on a technical scale. In polymerization processes, on a technical scale, it is preferred, therefore, to use as a solvent the low-priced aliphatic hydrocarbons or 15 mixtures thereof, as marketed by the petrochemical industry. If an aliphatic hydrocarbon is used as solvent, the solvent may yet contain minor quantities of aromatic hydrocarbon, for instance toluene. Thus, if for instance methyl aluminoxane (MAO) is used as co- 20 catalyst, toluene can be used as solvent in order to supply the MAO in dissolved form to the polymerization reactor. Drying or purification is desirable if such solvents are used; this can be done without problems by the average person skilled in the art.

25 If the polymerization is carried out under pressure, the yield of polymer can be increased additionally, resulting in an even lower catalyst residue content. Chain regulators can be used to control the molecular weight and the amount of 30 unsaturation of the resulting copolymer. Preference is given to hydrogen as the chain regulator.

The polymerization can also be performed in several steps, in series as well as in parallel. If required, the catalyst composition, temperature, 35 hydrogen concentration, pressure, residence time, etc. may be varied from step to step. In this way it is also

possible to obtain products with a wide molecular weight distribution.

The polymer solution resulting from the polymerization can be worked up by a method known per se. In general the catalyst is de-activated at some point during the processing of the polymer. The de-activation is also effected in a manner known per se, e.g. by means of water or an alcohol. Removal of the catalyst residues can mostly be omitted because the quantity of catalyst in the polymer, in particular the content of halogen and transition metal is very low at this point owing to the use of the catalyst system in the process according to the invention.

The copolymers, prepared according to the process of the present invention, can be used in different applications, like impact modifications, use in extrusion coating and wire-and-cable applications. These polymers are also useful in the manufacture of rubber articles and modified rubber articles.

The invention will now be elucidated by means of the following non-restrictive examples.

In the following: "Cp" means "cyclopentadienyl"; "Me" means "methyl"; "Bu" means "butyl"; "ⁱPr" means "isopropyl".

25

EXAMPLES

Synthesis of bidentate monocyclopentadienyl complexes

Example I

30 Synthesis of (dimethylaminoethyl)tetramethyl-cyclopentadienyltitanium(III)dichloride
(CpMe₂(CH₂)₂NMe₂TiCl₂).

a) Preparation of 4-hydroxy-4-(dimethylamino-ethyl)-

3,5-dimethyl-2,5-heptadiene

35 (7. 2-bromo-2-butene (108 g; 0.800 mol) was added

5 to 10.0 g of lithium (1.43 mol) in diethyl ether (300 mL) in about 30 minutes with reflux. After stirring overnight (17 hours), ethyl-3-(N,N-dimethylamino)propionate (52.0 g; 0.359 mol) was added to the reaction mixture in about 15 minutes. After stirring for 30 minutes at room temperature 200 mL of water was added dropwise. After separation, the water phase was extracted two times with 10 50 mL of CH_2Cl_2 . The organic phase was boiled down and the residue was distilled at reduced pressure. The yield was 51.0 g (67%).

15 b) Preparation of (dimethylaminoethyl)tetramethyl-
cyclopentadiene

20 The carbinol (21.1 g; 0.10 mol) prepared as described under a) was added in a single portion to p-toluenesulphonic acid. H_2O (28.5 g; 0.15 mol), dissolved in 200 mL of diethyl ether. After stirring for 30 minutes at room temperature, the reaction mixture was poured out in a solution of 50 g of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ in 250 mL of water. After separation, the water phase was extracted two times with 100 mL of diethyl ether. The combined ether layer was dried (Na_2SO_4), filtered and 25 boiled down. Then the residue was distilled at reduced pressure. The yield was 11.6 g (60%).

30 c) Preparation of (dimethylaminoethyl)tetramethyl-
cyclopentadienyltitanium(III)dichloride

35 1.0 equivalent of n-BuLi (1.43 mL; 1.6 M) was added (after cooling to -60°C) to a solution of the $\text{C}_5\text{Me}_4\text{H}(\text{CH}_2)_2\text{NMe}_2$ of b) (0.442 g; 2.29 mmol) in THF (50 mL), after which the cooling bath was removed. After warming to room temperature, the solution was cooled to -100°C and then $\text{TiCl}_3 \cdot 3\text{THF}$ (0.85 g; 2.3 mmol) was added in a single portion. After stirring for 2 hours at room

temperature, the THF was removed at reduced pressure. After addition of special boiling point gasoline, the complex (a green solid) was purified by repeated washing of the solid, followed by filtration and back 5 distillation of the solvent. It was also possible to obtain the pure complex through sublimation.

Example II

10 Synthesis of (dibutylaminoethyl)tetramethyl-
cyclopentadienyltitanium(III) dichloride
(CpMe₄(CH₂)₂NBu₂TiCl₂).

a) Preparation of ethyl 3-(N,N-di-n-
butylamino)propionate

15 Ethyl 3-bromopropionate (18.0 g; 0.10 mol) was added carefully to di-n-butylamine (25.8 g; 0.20 mol), followed by stirring for 2 hours. Then diethyl ether (200 mL) and pentane (200 mL) were added. The precipitate was filtered off, the filtrate was boiled 20 down and the residue was distilled at reduced pressure. The yield was 7.0 g (31%).

b) Preparation of bis(2-butenyl)(di-n-butylaminoethyl)-
methanol

25 2-Lithium-2-butene was prepared from 2-bromo-2-butene (16.5 g; 0.122 mol) and lithium (2.8 g; 0.4 mol) as in Example I. To this, the ester of a) (7.0 g; 0.031 mol) was added with reflux in approx. 5 minutes, followed by stirring for about 30 minutes. Then water 30 (200 mL) was carefully added dropwise. The water layer was separated off and extracted twice with 50 ml of CH₂Cl₂. The combined organic layer was washed once with 50 mL of water, dried (K₂CO₃), filtered and boiled down. The yield was 9.0 g (100%).

35

c) Preparation of (di-n-butylaminoethyl)tetramethyl-

cyclopentadiene)

4.5 g (0.015 mol) of the carbinol of b) was added dropwise to 40 mL of concentrated sulphuric acid of 0°C, followed by stirring for another 30 minutes at 5 0°C. Then the reaction mixture was poured out in a mixture of 400 mL of water and 200 mL of hexane. The mixture was made alkaline with NaOH (60 g) while being cooled in an ice bath. The water layer was separated off and extracted with hexane. The combined hexane 10 layer was dried (K_2CO_3), filtered and boiled down. The residue was distilled at reduced pressure. Boiling point 110°C (0.1 mm Hg). The yield was 2.3 g (55%).

d) Preparation of (di-n-
15 butylaminoethyl)tetramethylcyclo-
pentadienyltitanium(III)dichloride

1.0 equivalent of n-BuLi (0.75 mL; 1.6 M) was added (after cooling to -60°C) to a solution of the $C_5Me_4H(CH_2)_2NBu_2$ of c) (0.332 g; 1.20 mmol) in THF (50 20 mL), after which the cooling bath was removed. After warming to room temperature, the solution was cooled to -100°C and then $TiCl_3 \cdot 3THF$ (0.45 g; 1.20 mmol) was added in a single portion. After stirring for 2 hours at room temperature, the THF was removed at reduced 25 pressure. The purification was done as in Example I.

Example III

The catalyst is (dimethylaminomethyl)-
diisopropyl-cyclopentadienyltitanium-(III) dichloride
30 ($CpH_2^1Pr_2(CH_2)_2NMe_2TiCl_2$).

a. Preparation of di(2-propyl)cyclopentadiene

In a double-walled reactor having a volume of 200 mL, provided with baffles, condenser, top stirrer, 35 thermometer and dropping funnel, 180 g of clear 50% strength NaOH (2.25 mol), 9.5 g of Aliquat 336 (23

mmol) and 15 g (0.227 mol) of freshly cracked cyclopentadiene were combined. The reaction mixture was stirred turbulently at a speed of 1385 rpm for a few minutes. Then 56 g of 2-propyl bromide (0.46 mol) were 5 added, cooling with water taking place at the same time. A few minutes after the addition of the 2-propyl bromide the temperature rose by approximately 10°C. Stirring then continued for 6 hours at 50°C. GC was used to show that at that instant 92% of di(2- 10 propyl)cyclopentadiene was present in the mixture of di-and tri(2-propyl)cyclopentadiene. The product was distilled at 10 mbar and 70°C. After distillation, 25.35 g of di(2-propyl)cyclopentadiene were obtained. Characterization took place with the aid of GC, GC-MS, 15 ^{13}C -and ^1H -NMR.

b. Preparation of (dimethylaminoethyl)tri(2-propyl)-cyclopentadiene

In a dry 500 mL three-necked flask with a 20 magnetic stirrer, a solution of 62.5 mL of *n*-butyllithium (1.6M in *n*-hexane; 100 mmol) was added under a dry nitrogen atmosphere to a solution of 19.2 g (100 mmol) of triisopropyl-cyclopentadiene in 250 mL of THF at -60°C. After heating to room temperature (in 25 approximately 1 hour) stirring continued for a further 2 hours. After cooling to -60°C, a solution of (dimethylaminoethyl) tosylate (105 mmol) prepared in situ was added over a period of 5 minutes. The reaction mixture was heated to room temperature, followed by 30 overnight stirring. After addition of water, the product was extracted with petroleum ether (40-60°C). The combined organic layer was dried (Na_2SO_4) and evaporated under reduced pressure. The conversion was 97%. The dimethylamino- 35 ethyldiisopropylcyclopentadiene was obtained by distillation, with a yield of 54%.

c. Synthesis of [1-(dimethylaminoethyl)-2,4-di(2-propyl)cyclopentadienyltitanium(III) dichloride
[C₅H₂(iPr)₂(CH₂)₂NMe₂Ti(III)Cl₂]

To 8.9 g (40.3 mmol) of (dimethylaminoethyl)-
5 di-(2-propyl)cyclopentadiene in 100 mL of
tetrahydrofuran in a 250 mL 3-necked flask, 25.2 mL of
n-butyllithium (1.6M, 40.3 mmol) were added dropwise.
In a second (500 mL) 3-necked flask, 100 ml of
tetrahydrofuran were added to 14.93 g (40.3 mmol) of
10 Ti(III)Cl₃.3THF. Both flasks were cooled to -60°C and
the organolithium compound was then added to the
Ti(III)Cl₃ suspension. The reaction mixture containing
1-(dimethylaminoethyl)-2,4-di(2-
propyl)cyclopentadienyltitanium(III) dichloride was
15 slowly brought to room temperature, after which
stirring was continued for a further 18 hours.

Polymerisations

The catalysts given in Examples I, II and III
20 were methylated with MeLi in diethylether.

A number of continuous streams of petrol,
propylene, ethylene catalyst and co-catalyst were dosed
to a 1-litre reactor. The solution was continuously
removed from the reactor. The catalyst was inactivated
25 with the aid of isopropyl alcohol in a flash vessel;
the monomers were flashed and the solution was
stabilised with the aid of about 1000 ppm of Irganox
1076®. The polymer was analysed after further
processing.

30

Analysis of the polymers

The composition of the polymers was
determined with the aid of Fourier Transform Infrared
Spectroscopy (FT-IR). The FT-IR results indicate the
35 composition of the various monomers in weight
percentages relative to the overall composition.

The polymers prepared according to the Examples were analysed by means of SEC-DV. Molecular weight distributions were determined according to the universal calibration principle as known from

5 literature (see Z. Grubistic, R. Rempp, H. Benoit, J. Polym. Sci., part B, 5, 753 (1967)).

The intrinsic viscosity (IV) was determined in decaline at 135°C.

10 The catalysts given in Examples I, II and III were methylated with MeLi in diethylether.

Polymerizations

Continuous streams of petrol, propylene, 15 ethylene, catalyst and co-catalyst were dosed to a 1-litre reactor. The solution was continuously removed from the reactor. The catalyst was inactivated with the aid of isopropyl alcohol in a flash vessel; the monomers were flashed and the solution was stabilised 20 with the aid of about 1000 ppm of Irganox 1076®. The polymer was analysed after further processing.

Analysis of the polymers

The composition of the polymers was 25 determined with the aid of Fourier Transform Infrared Spectroscopy (FT-IR). The FT-IR results indicate the composition of the various monomers in weight percentages relative to the overall composition.

The polymers prepared according to the 30 Examples were analysed by means of SEC-DV. Molecular weight distributions were determined according to the universal calibration principle as described in Z. Grubistic, R. Rempp, H. Benoit, J. Polym. Sci., part B, 5, 753 (1967), the complete disclosure of which is 35 incorporated herein by reference.

The intrinsic viscosity (int.visc. or "IV"

was determined in decaline at 135°C.

Examples IV-VIII

Table 1 presents the polymerization conditions of the continuous polymerization of ethylene and propylene for Examples IV-VIII. This Table indicates: the amounts of petrol, propylene and ethylene, the amount of catalyst added, the amount of co-catalyst, the polymerization temperature and the polymerization time.

Different catalysts have been used in the Examples: catalyst a is $\{\text{Cp}(\text{Me})_4(\text{CH}_2)_2\text{NMe}_2\}\text{TiMe}_2$, catalyst b is $\{\text{Cp}(\text{Me})_4(\text{CH}_2)_2\text{NBu}_2\}\text{TiMe}_2$, and catalyst c is $\{\text{CpH}_2^1\text{Pr}_2(\text{CH}_2)_2\text{NMe}_2\}\text{TiMe}_2$

15 (as they are prepared according to Examples I-III). The co-catalyst used in the Examples is dimethylanilinium tetrakis(pentafluorophenyl)borate $[\text{HMe}_2\text{N-C}_6\text{H}_5]^{+}[(\text{C}_6\text{F}_5)_4\text{B}]^{-}$

The results of the continuous polymerizations according to Examples IV-VIII are summarized in Table 2. This Table indicates: the polymer production (yield, expressed in grams/hour), the catalyst activity (expressed in kgram polymer/gram transition metal), the composition of the polymer determined with the aid of 25 FT-IR (expressed in weight percentages), the intrinsic viscosity of the copolymer, the number average molecular weight (M_n), the weight average molecular weight (M_w) and the absolute molecular weight distribution ($MWD = M_w/M_n$), determined with the aid of 30 SEC-DV.

Some examples of transition metal complexes useful in the process according to the invention are presented in Table 3.

TABLE 1. EXPERIMENTAL CONDITIONS

Example	petrol (kg/h)	propyl- ene (g/h)	ethyl- ene (g/h)	cat. type	cat. (mmol/h)	co-cat. (mmol/h)	pol. temp. (°C)	pol. time (min)
IV	2.22	652	319	a	0.026	0.1	158	10
V	2.02	756	419	a	0.022	0.2	153	9
VI	2.34	412	445	a	0.020	0.08	123	10
VII	2.16	705	336	b	0.047	0.1	148	10
VIII	2.04	839	317	c	0.2	0.4	148	10

TABLE 2. RESULTS OF THE POLYMERIZATIONS AND
RESULTS OF ANALYSIS OF THE COPOLYMERS OBTAINED

Example	Yield (g/h)	activity (kg/g)	%C3 (wt%)	IV (dl/g)	M _n (kg/mol)	M _w (kg/mol)	MWD
IV	71.0	570	54	0.45	12	31	2.6
V	63.0	600	50	0.98	27	63	2.3
VI	63.0	660	43	1.5	48	120	2.5
VII	64.0	280	54	0.79	nd	nd	nd
VIII	66.0	70	57	0.25	7	20	2.8

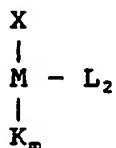
nd = not determined

TABLE 3. EXAMPLES OF TRANSITION METAL COMPLEXES USEFUL IN THE PROCESS
ACCORDING TO THE INVENTION (SEE FORMULAS I-V)

M[e]	L	Y	R	D	R'	R"	R'''
T1	C1	C ₅ H ₄	dimethylsilyl	N	methyl	L	
Zr	P	C ₅ Me ₄	diethylsilyl	P	ethyl	T-R'	
Hf	Br	Indenyl	dipropylsilyl	As	propyl	X	
V	I	Fluorenyl	di butylsilyl	Sb	n-butyl	diethyl ether	
Nb	methyl	benzotriuorenyl	methylamido	O	n-pentyl	tetrahydrofuran	
Ta	methoxy	octahydrofluorenyl	dimethylgermynyl	S	methoxy	trimethylamine	
Cr	ethoxy	C ₅ H ₃ (H-Bu)	diethylgermynyl	Se	ethoxy	triethylamine	
Mo	hydride	tetrahydroindenyl	diethylpropylene	Cl		trimethylphosphine	
W	isopropyl	C ₅ H ₃ (SiMe ₃)	tetramethylidiloxane			triethylphosphine	
	octyl	methylamido	diphenylsilyl	P		triphenylphosphine	
	propoxy	phenyl-phosphido	tetramethylsilaethylene	Br		dimethylsulphide	
	phenoxy		methylene	I		dimethylaniline	
	benzyl		diethylmethylene			phenoxy	
	methylthio		ethylen			benzyl	
			dimethyllethylene			H	
			ethylphosphido				
			phenylphosphido				

WHAT IS CLAIMED IS:

1. A process for the preparation of an ethylene/α-olefin copolymer with an ethylene content of between 20 and 90 weight %, by the step of conducting polymerization of ethylene and at least one α-olefin under effective copolymerization conditions at a temperature of between about 100°C and about 220°C, in the presence of a catalyst comprising a reduced transition metal complex and a co-catalyst, wherein said reduced transition metal complex has the following structure:



wherein:

M is a reduced transition metal selected from group 4, 5 or 6 of the Periodic Table of the Elements;

X is a multidentate monoanionic ligand represented by the formula $(Ar-R_t-)_n Y(-R_t-DR'_n)_q$;

Y is a member selected from the group consisting of a cyclopentadienyl, amido $(-NR'-)$, and phosphido $(-PR'-)$ group;

R is at least one member selected from the group consisting of (i) a connecting group between the Y group and the DR'_n group and (ii) a connecting group between the Y group and the Ar group, wherein when the ligand X contains more than one R group, the R groups can be identical as or different from each other;

D is an electron-donating hetero atom selected from group 15 or 16 of the Periodic Table of Elements;

R' is a substituent selected from the group consisting of a hydrogen, hydrocarbon radical and hetero atom-containing moiety, except that R' cannot be hydrogen when R' is directly bonded to the electron-donating hetero atom D, wherein when the multidentate monoanionic ligand X contains more than one substituent R', the substituents R' can be identical or different from each other;

Ar is an electron-donating aryl group;

L is a monoanionic ligand bonded to the reduced transition metal M, wherein the monoanionic ligand L is not a ligand comprising a cyclopentadienyl, amido (-NR'-), or phosphido (-PR'-) group, and wherein the monoanionic ligands L can be identical or different from each other;

K is a neutral or anionic ligand bonded to the reduced transition metal M, wherein when the transition metal complex contains more than one ligand K, the ligands K can be identical or different from each other;

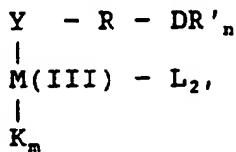
m is the number of K ligands, wherein when the K ligand is an anionic ligand m is 0 for M^{3+} , m is 1 for M^{4+} , and m is 2 for M^{5+} , and when K is a neutral ligand m increases by one for each neutral K ligand;

n is the number of the R' groups bonded to the electron-donating hetero atom D, wherein when D is selected from group 15 of the Periodic Table of Elements n is 2, and when D is selected from group 16 of the Periodic Table of Elements n is 1;

q and s are the number of $(-R_t-DR'_n)$ groups and $(Ar-R_t-)$ groups bonded to group Y, respectively, wherein q + s is an integer not less than 1; and

t is the number of R groups connecting each of (i) the Y and Ar groups and (ii) the Y and DR'_n groups, wherein t is selected independently as 0 or 1.

2. A process according to claim 1, wherein the Y group is a cyclopentadienyl group.
3. A process according to claim 2, wherein the cyclopentadienyl group is an unsubstituted or substituted indenyl, benzoindenyl, or fluorenyl group.
4. A process according to claim 2, wherein said reduced transition metal complex has the following structure:



wherein:

M(III) is a transition metal from group 4 of the Periodic Table of the Elements in oxidation state 3+.

5. A process according to claim 2, wherein said reduced transition metal is titanium.
6. A process according to claim 2, wherein said electron-donating hetero atom D is nitrogen.
7. A process according to claim 2, wherein the R' group in the DR'_n group is an n-alkyl group.
8. A process according to claim 2, wherein said R group has the following structure:

$(-\text{CR}'_2^-)_p$,

wherein p is 1, 2, 3, or 4.

9. A process according to claim 2, wherein said monoanionic ligand L is selected from the group consisting of a halide, an alkyl group, and a benzyl group.
10. A process according to claim 2, wherein the Y group is a di-, tri- or tetraalkyl-cyclopentadienyl.
11. A process according to claim 2, wherein said co-catalyst comprises a linear or cyclic aluminoxane or a triaryl borane or tetraaryl borate.
12. A process according to claim 2, wherein at least one member selected from the group consisting of said reduced transition metal complex and said co-catalyst is supported on at least one carrier.
13. The process according to claim 1, wherein a copolymer with a number average molecular weight M_n of between 100 and 1,000,000 is prepared.
14. The process according to claim 1, wherein a copolymer with a number average molecular weight M_n of between 100 and 30,000 is prepared.
15. The process according to claim 3, wherein said copolymer is prepared at a temperature of between 135 and 220°C.
16. The process according to claim 1, wherein a copolymer with a number average molecular weight M_n of between 20,000 and 100,000 is prepared.
17. The process according to claim 16, wherein said copolymer is prepared at a temperature of between 115 and 180°C.
18. The process according to claim 1, wherein the polymerization is conducted at a pressure of below 100 MPa.
19. The process according to claim 1, wherein the α-

olefin is a member selected from the group consisting of propylene, 1-butene, 1-hexene, 1-octene, and any combinations thereof.

20. The process according to claim 21, wherein the α -olefin is propylene.

1/1

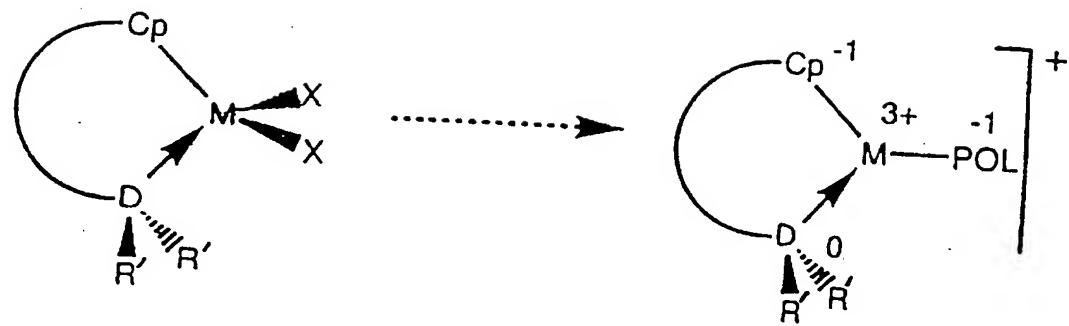


FIG. 1

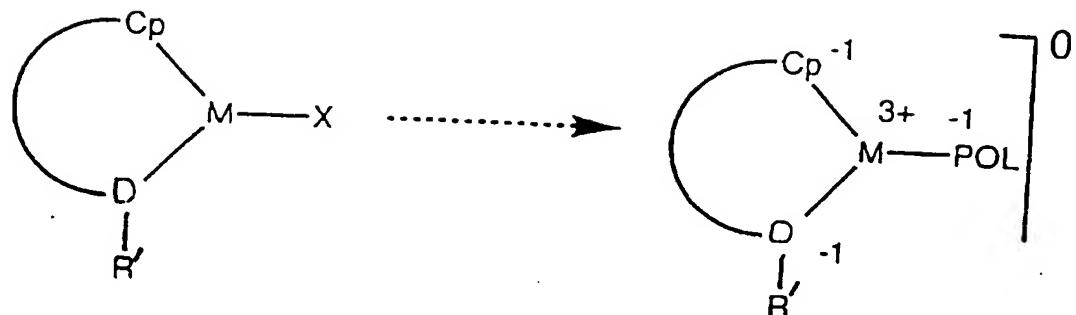


FIG. 2

INTERNATIONAL SEARCH REPORT

Int. Application No
PCT/NL 97/00243

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F212/04 C08F4/64

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 96 13529 A (DSM NV) 9 May 1996 * claims; page 13, line 33 to page 14, line 4; page 15, lines 25-28; page 16, lines 4-15 * ---	1-20
A	EP 0 416 815 A (DOW CHEMICAL CO) 13 March 1991 * claims 6-24, 26-28; page 11, lines 32-38; page 17, example 4 * ---	1-20
A	WO 93 08221 A (DOW CHEMICAL CO) 29 April 1993 * claims; page 31, line 4 to page 32, line 8; examples * ---	1-20
A	WO 93 19104 A (DOW CHEMICAL CO) 30 September 1993 * claims; page 12, line 27; examples * -----	1-20

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

1

Date of the actual completion of the international search

3 June 1997

Date of mailing of the international search report

26.06.97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+ 31-70) 340-3016

Authorized officer

Mergoni, M

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/NL 97/00243

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO 9613529 A	09-05-96	AU 3817595 A		23-05-96
EP 0416815 A	13-03-91	AU 645519 B		20-01-94
		AU 6203990 A		07-03-91
		CA 2024333 A		01-03-91
		EP 0764653 A		26-03-97
		EP 0764664 A		26-03-97
		EP 0764654 A		26-03-97
		EP 0774468 A		21-05-97
		EP 0765888 A		02-04-97
		HU 209316 B		28-04-94
		JP 7053618 A		28-02-95
		JP 7070223 A		14-03-95
		JP 2535249 B		18-09-96
		JP 3163088 A		15-07-91
		NO 176964 B		20-03-95
		NO 179043 B		15-04-96
		NO 954469 A		01-03-91
		CN 1049849 A,B		13-03-91
		PL 166689 B		30-06-95
WO 9308221 A	29-04-93	US 5272236 A		21-12-93
		US 5278272 A		11-01-94
		CA 2120766 A		29-04-93
		EP 0608369 A		03-08-94
		FI 941727 A		31-05-94
		JP 7500622 T		19-01-95
		US 5380810 A		10-01-95
		US 5427807 A		27-06-95
		US 5562958 A		08-10-96
		US 5395471 A		07-03-95
		US 5582923 A		10-12-96
		US 5525695 A		11-06-96
		US 5591390 A		07-01-97
		US 5595705 A		21-01-97
WO 9319104 A	30-09-93	US 5374696 A		20-12-94
		CA 2117689 A		30-09-93
		EP 0632819 A		11-01-95
		FI 944423 A		23-09-94

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/NL 97/00243

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9319104 A		US 5494874 A	27-02-96
		US 5532394 A	02-07-96

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.